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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: K. TAKEUCHI, et al.  
Serial No.: 10/591,696  
Filed: SEPTEMBER 5, 2006  
For: PREPREG, METAL-CLAD LAMINATE AND PRINTED CIRCUIT BOARD USING SAME  
Group AU: 1794  
Examiner: Camie S. Thompson  
Confirm. No: 3031

**SUBMISSION OF VERIFIED ENGLISH TRANSLATIONS OF  
JAPANESE PRIORITY APPLICATIONS**

**Mail Stop: AMEND – NO FEE**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

July 25, 2008

Sir:

The English translations of the four (4) Japanese priority applications for the above-identified application, submitted with the Amendment filed July 7, 2008, and referred to on page 13 of this Amendment filed July 7, 2008, are noted. These four (4) English translations were submitted without verification as to the accuracy thereof, in the Amendment filed July 7, 2008.

In view of the foregoing, enclosed please find copies of the aforementioned English translations, together with respective Verifications as to the accuracy of the translations. In view of the enclosed Verifications, together with the attached English translations, and previously submitted Claims for Priority, it is respectfully submitted that all applicable requirements of 37 CFR 1.55 have been satisfied, in connection

with Applicants being accorded benefit of the filing dates of the aforementioned Japanese priority applications.

Moreover, attention is respectfully directed to United States Patent Application Publication No. 2004/0258899, published December 23, 2004, which is a prior publication of U.S. Patent No. 7,138,174, applied in rejecting claims in the Office Action mailed February 6, 2008, in the above-identified application. The Japanese priority applications for the above-identified application have an earlier filing date than the publication date of No. 2004/0258899. As all applicable requirements of 37 CFR 1.55 and 35 USC 119 have been satisfied in view of present submission of the English translations of these Japanese priority applications together with respective Verifications of the accuracy thereof, it is respectfully submitted that No. 2004/0258899 is not prior art under 35 USC 102(a), and is, at most, prior art under 35 USC 102(e); and, in view of the Statement at the bottom of page 12 of the Amendment filed July 7, 2008, is disqualified as prior art under 35 USC 103.

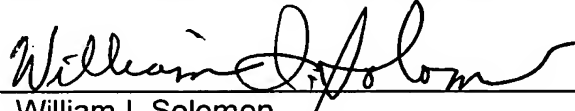
In view of the foregoing, with filing of the enclosed English translations together with Verifications of the accuracy thereof; and in light of the comments and amendments in the Amendment filed July 7, 2008, reconsideration and allowance of all claims presently pending in the above-identified application are respectfully requested.

To the extent necessary, Applicants hereby petition for an extension of time under 37 CFR 1.136. Kindly charge any shortage of fees due in connection with the filing of this paper, including any extension of time fees, to the Deposit Account of

Antonelli, Terry, Stout & Kraus, LLP, Account No. 01-2135 (case 1303.46565X00),  
and please credit any overpayments to such Deposit Account.

Respectfully submitted,

**ANTONELLI, TERRY, STOUT & KRAUS, LLP**

By   
William I. Solomon  
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Attachments: Verified English translations of the 4 Japanese Priority Documents

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VERIFICATION

The undersigned, of the below address, hereby certifies that he/she well knows both the English and Japanese languages, and that the attached is an accurate English translation of the Japanese Patent application filed on March 4, 2004 under No. P2004-060582.

The undersigned declares further that all statements made herein of his/her own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 4th day of July, 2008.

Signature:

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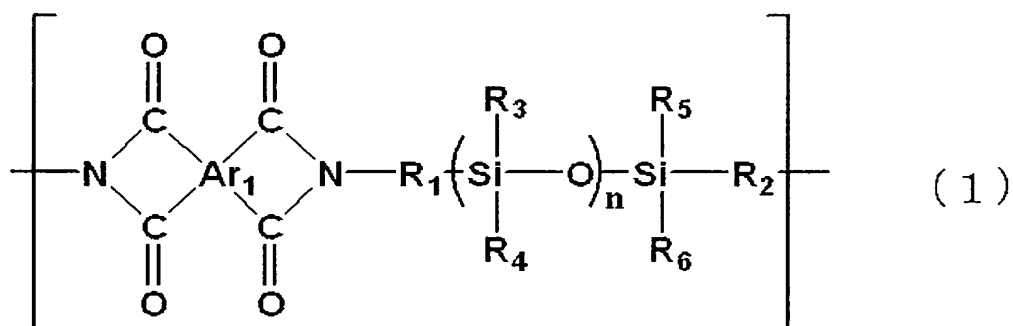
[Document Name] Claims

[Claim 1] A prepreg obtained by impregnating a resin composition comprising a resin with an imide structure and a thermosetting resin into a fiber base material with a thickness of 5-50  $\mu\text{m}$ .

5 [Claim 2] A prepreg according to claim 1, wherein said resin with an imide structure has a siloxane structure.

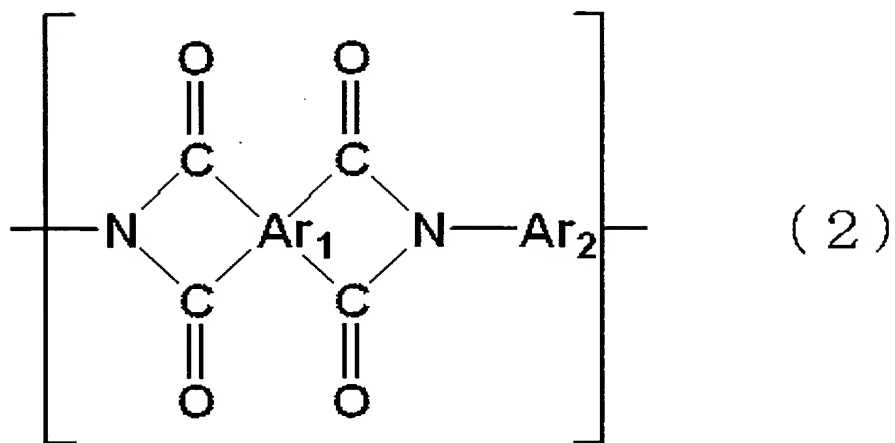
[Claim 3] A prepreg according to claim 1 or 2, wherein said resin with an imide structure is a polyimide resin having the structure represented by the following general formula (1) or the structure represented by the following general formula (2).

10 [Chemical Formula 1]



[wherein  $\text{Ar}^1$  represents a tetravalent aromatic group,  $\text{R}^1$  and  $\text{R}^2$  represent a divalent hydrocarbon group,  $\text{R}^3 - \text{R}^6$  represent a C1-6 hydrocarbon group, and  $n$  represents an integer of 1-50.]

15 [Chemical Formula 2]



[wherein Ar<sup>1</sup> represents a tetravalent aromatic group and Ar<sup>2</sup> represents a divalent aromatic group.]

[Claim 4] A prepreg according to any one of claims 1 to 3, wherein  
5 said thermosetting resin is an epoxy resin.

[Claim 5] A metal foil-clad laminate obtained by stacking a prepreg  
according to any one of claims 1 to 4 and a metal foil, and subjecting  
the stack to heat and pressure.

[Claim 6] A printed circuit board obtained by forming a circuit on said  
10 metal foil-clad laminate according to claim 5.

[Document Name] Specification

[Title of the Invention] PREPREG, METAL CLAD LAMINATE,  
AND PRINTED CIRCUIT BOARD USING SAME

[Field of the Invention]

5 [0001]

The present invention relates to a prepreg and to a metal foil-clad laminate and printed circuit board that employ it.

[Prior Art]

[0002]

10 Laminates for printed circuit boards are formed by stacking a prescribed number of prepregs comprising an electrical insulating resin composition as the matrix, and subjecting them to heat and pressure for integration.

15 Metal-clad laminates are used for formation of printed circuits by a subtractive process. Metal-clad laminates are fabricated by stacking a metal foil such as copper foil on a surface (either or both surfaces) of a prepreg and subjecting the stack to heat and pressure. As electrical insulating resins there are commonly used thermosetting resins such as phenol resins, epoxy resins, polyimide resins, bismaleimide-triazine  
20 resins and the like. Thermoplastic resins such as fluorine resins or polyphenylene ether resins are also sometimes used.

[0003]

25 On the other hand, with the increasing popularity of data terminal devices such as personal computers and cellular phones there is a trend toward miniaturization and high-densification of the printed circuit boards mounted therein. The mounting methods are advancing

from pin-insertion types to surface-mounted types, and also to area array types of which BGA (ball grid arrays) using plastic boards are a typical example. In boards where bare chips such as BGA are directly mounted, connection between the chips and boards is commonly achieved by wire bonding using thermosonic bonding. In such cases, the board on which the bare chip is mounted is exposed to high temperatures of 150°C and above, and therefore the electrical insulating resin must have some degree of heat resistance.

[0004]

As lead-free solders become more common for environmental reasons, the melting points of solders are increasing as a result. Thus, even higher heat resistance is demanded for boards. Demand for halogen-free materials is also increasing, thus precluding the use of bromine-based flame retardants. Moreover, so-called the "repair properties" allowing mounted chips to be removed are often required. During repair, the boards are subjected to about the same level of heating as during chip mounting, after which further heat treatment is carried out for remounting of chips. Thus, boards exhibiting repair properties must also have cycling heat shock-resistant properties at high temperatures. Peeling between the fiber material and resin has often resulted in conventional insulating resin systems.

[0005]

Prepregs have been proposed that exhibit excellent heat shock resistance, reflow resistance and crack resistance, and improved microwiring formation properties, by impregnating a resin composition comprising a polyamideimide as an essential component



into the fiber material (see Patent Literature 1). The base having thermal resistance obtained by impregnating the resin composition comprising a silicon-modified polyimide resin and thermosetting resin into the fiber material is proposed (see Patent Literature 2). Also, with the trend toward greater miniaturization and higher performance of electronic devices, it is becoming necessary to house part-mounted printed circuit boards in increasingly limited spaces. This is accomplished by methods of arranging multiple printed circuit boards in stacks and connecting them alternately with wire harnesses or flexible wiring boards. There are also used rigid-flex boards which are layered combinations of polyimide-based flexible boards and conventional rigid boards.

[Patent Literature 1] Japanese Unexamined Patent Publication No. 2003-55486

[Patent Literature 2] Japanese Unexamined Patent Publication No. H08-193139

[Disclosure of the Invention]

[Problem to be Solved by the Invention]

[0006] The present invention solves the problems of the prior art described above, and is to provide a printed circuit board with excellent dimensional stability and heat resistance and the ability to be bent and housed at high density in electronic device packages, by impregnating a thin fiber base material with a resin having excellent adhesion with metal foils or fiber base materials, excellent heat resistance and high pliability, as well as to provide a prepreg and metal foil-clad laminate which yield said printed circuit board.

[Means for Solving the Problem]

[0007]

The present invention relates to the following.

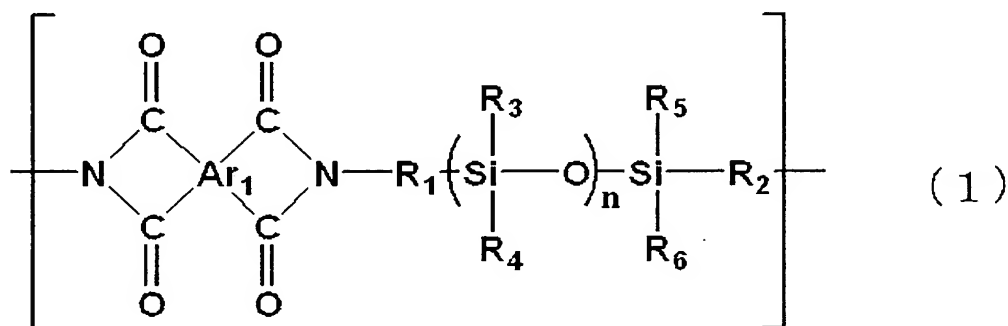
(1) A prepreg obtained by impregnating a resin composition comprising a resin with an imide structure and a thermosetting resin into a fiber base material with a thickness of 5-50  $\mu\text{m}$ .

(2) A prepreg according to (1), wherein said resin with an imide structure has a siloxane structure.

(3) A prepreg according to (1) or (2), wherein said resin with an imide structure is a polyimide resin having the structure represented by the following general formula (1) or the structure represented by the following general formula (2).

[0008]

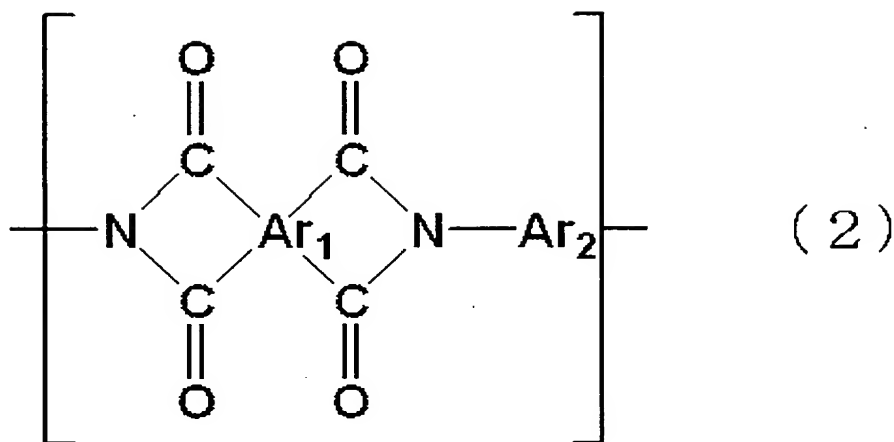
[Chemical Formula 1]



[wherein  $\text{Ar}^1$  represents a tetravalent aromatic group,  $\text{R}^1$  and  $\text{R}^2$  represent a divalent hydrocarbon group,  $\text{R}^3 - \text{R}^6$  represent a C1-6 hydrocarbon group, and  $n$  represents an integer of 1-50.]

[0009]

[Chemical Formula 2]



[wherein Ar<sup>1</sup> represents a tetravalent aromatic group and Ar<sup>2</sup> represents a divalent aromatic group.]

(4) A prepreg according to any one of (1) to (3), wherein said thermosetting resin is an epoxy resin.

(5) A metal foil-clad laminate obtained by stacking a prepreg according to any one of (1) to (4) and a metal foil, and subjecting the stack to heat and pressure.

(6) A printed circuit board obtained by forming a circuit on the metal foil of a metal foil-clad laminate according to (5).

[Effects of the Invention]

[0010]

The metal foil-clad laminate and the printed circuit board obtained by using the prepreg of the present invention have the ability to be bent and have excellent dimensional stability and heat resistance. This prepreg can be housed at high density in electronic device packages because of the ability to be bent arbitrarily when manufacturing the printed circuit board.

[Best Mode for Carrying Out the Invention]

[0011]

The prepreg of the present invention is the prepreg obtained by impregnating a resin composition comprising a resin with an imide structure and a thermosetting resin into a fiber base material with a thickness of 5-50  $\mu\text{m}$ . The polyimide resin having a siloxane structure is preferred as the resin with an imide structure. The polyimide resin obtained by reacting diamine with tetracarboxylic acid dianhydrides is more preferred as the resin with an imide structure of the present invention. The polyimide resin of the present invention is a polyimide resin having a siloxane structure. As the polyimide resin having a siloxane structure, the polyimide resins having a structure represented by general formula (1) or having a structure represented by general formula (1) and general formula (2).

[0012]

Examples of tetracarboxylic acid dianhydrides include 3,3',4,4'-diphenylethertetracarboxylic dianhydride, 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 2,2',3,3'-benzophenonetetracarboxylic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 2,3,3',4'-biphenyltetracarboxylic dianhydride, pyromellitic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, 1,4,5,6-naphthalenetetracarboxylic dianhydride, 3,4,9,10-perylenetetracarboxylic dianhydride, 3,3,6,7-anthracenetetracarboxylic dianhydride, 1,2,7,8-

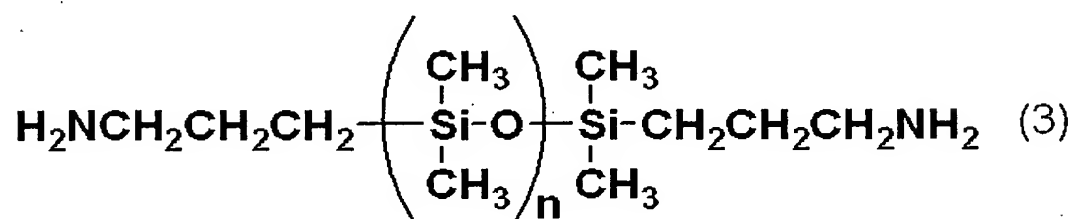
phenanthrenetetracarboxylic dianhydride and 4,4'-(hexafluoroisopropylidene)phthalic dianhydride.

[0013]

As diamines used in present invention there may be mentioned  
 5 siloxanediamines represented by the following general formulas (3)-(6).

[0014]

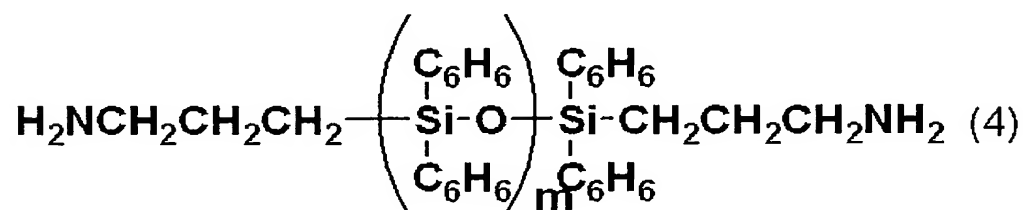
[Chemical Formula 3]



(n represents an integer of 1-50.)

[0015]

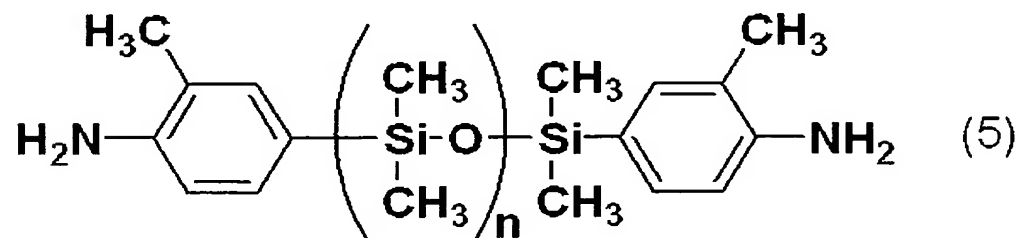
[Chemical Formula 4]



(n represents an integer of 1-50.)

[0016]

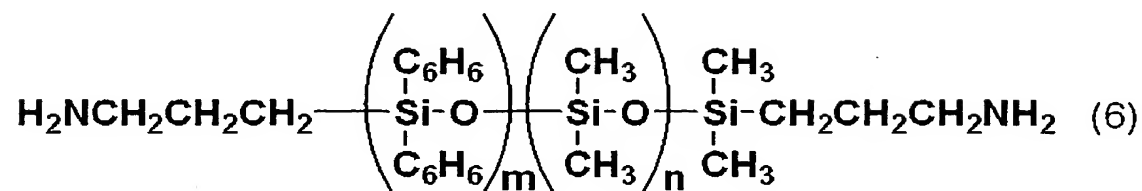
[Chemical Formula 5]



(n represents an integer of 1-50.)

[0017]

[Chemical Formula 6]



(n, m represent an integer of 1-49, n+m represents an integer of 50 or less.)

[0018]

Examples of siloxanediamines represented by general formula (3) above include X-22-161AS (450 amine equivalents), X-22-161A (840 amine equivalents), X-22-161B (1500 amine equivalents) (all products of Shin-Etsu Chemical Co., Ltd.), BY16-853 (650 amine equivalents) and BY16-853B (2200 amine equivalents) (all products of Dow Corning Toray Silicone Co., Ltd.). Examples of siloxanediamines represented by general formula (6) above include X-22-9409 (700 amine equivalents) and X-22-1660B-3 (2200 amine equivalents) (both products of Shin-Etsu Chemical Co., Ltd.).

[0019]

By introducing the siloxane structure into the polyimide resin, the base obtained by impregnating a resin composition into a fiber base material with a thickness of 5-50  $\mu\text{m}$  is bent easily when the base is cured.

[0020]

As the diamine used in the present invention, Combined use of siloxanediamines and aromatic diamines is preferred. Examples of aromatic diamines include m-phenylenediamine, p-phenylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylpropane, benzidine, 4,4'-diaminodiphenylsulfide, 4,4'-diaminodiphenylsulfone, 3,3'-diaminodiphenylsulfone, 4,4'-diaminodiphenyl ether, 4,4'-diamino-p-terphenyl, 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP), bis[4-(3-aminophenoxy)phenyl]sulfone, bis[4-(4-aminophenoxy)phenyl]sulfone, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, bis[4-(4-aminophenoxy)phenyl]methane, 4,4'-bis(4-aminophenoxy)biphenyl, bis[4-(4-aminophenoxy)phenyl]ether, bis[4-(4-aminophenoxy)phenyl]ketone, 1,3-bis(4-aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene, 2,2'-dimethylbiphenyl-4,4'-diamine, 2,2'-bis(trifluoromethyl)biphenyl-4,4'-diamine, 2,6,2',6'-tetramethyl-4,4'-diamine, 5,5'-dimethyl-2,2'-sulfonyl-biphenyl-4,4'-diamine, 3,3'-dihydroxybiphenyl-4,4'-diamine, (4,4'-diamino)diphenyl ether, (4,4'-diamino)diphenylsulfone, (4,4'-diamino)benzophenone, (3,3'-diamino)benzophenone, (4,4'-diamino)diphenylmethane, (4,4'-diamino)diphenyl ether and 3,3'-diaminodiphenyl ether.

#### [0021]

In preparing the polyimide resin having a siloxane structure, the blending ratio of the aromatic diamine "a" and the siloxanediamine "b" is preferably  $a/b=99.9/0.1-0/100$  (molar ratio), more preferably  $a/b=95/5-30/70$  and even more preferably  $a/b=90/10-50/50$ . If the blending proportion of the siloxanediamine "b" is large, the Tg will

tend to be reduced. If the blending proportion of the siloxanediamine "b" is small, a larger amount of varnish solvent will tend to remain in the resin composition from production of the prepreg.

[0022]

5 As thermosetting resins to be used for the invention there may be mentioned epoxy resins, polyimide resins, unsaturated polyester resins, polyurethane resins, bismaleimide resins, triazine-bismaleimide resins and phenol resins. The thermosetting resin is preferably used at 1-200 parts by weight with respect to 100 parts by weight of the polyimide resin. There are preferred glycidyl group-containing epoxy resins in 10 the present invention. The thermosetting resin is used at 1-200 parts by weight with respect to 100 parts by weight of the siloxane-modified polyimide resin in the present invention, if the content of the thermosetting resin is less than 1 part by weight, the solvent resistance will tend to be inferior, if it exceeds 200 parts by weight, the Tg will 15 be lower due to the unreacted thermosetting resin, leading to insufficient heat resistance and undesirable reduction in flexibility. Thus, the content of the thermosetting resin is more preferably 3-100 parts by weight and even more preferably 10-60 parts by weight to 20 100 parts by weight of the siloxane-modified polyimide resin.

[0023]

As epoxy resins there may be mentioned polyglycidyl ethers obtained by reacting epichlorhydrin with a polyhydric phenol such as bisphenol A, a novolac-type phenol resin or an orthocresol/novolac-type phenol 25 resin or with a polyhydric alcohol such as 1,4-buthane diol, polyglycidyl esters obtained by reacting epichlorhydrin with a



polybasic acid such as phthalic acid or hexahydrophthalic acid, N-glycidyl derivatives of compounds with amine, amide or heterocyclic nitrogenous bases, and alicyclic epoxy resins.

[0024]

5 By using an epoxy resin as the thermosetting resin in the present invention, it is possible to cure at a temperature of below 180°C, and to further improve the thermal, mechanical and electrical properties. It is preferred to use as the epoxy resin a combination of an epoxy resin with two or more glycidyl groups and its curing agent, a combination  
10 of an epoxy resin with two or more glycidyl groups and its curing accelerator, or a combination of an epoxy resin with two or more glycidyl groups and its curing agent and curing accelerator. A greater number of glycidyl groups is preferred, with 3 or more being more preferred. The content of the thermosetting resin will differ  
15 depending on the number of glycidyl groups, and the content may be lower with a larger number of glycidyl groups.

[0025]

The curing agent and curing accelerator for the epoxy resin are not particularly restricted so long as they react with the epoxy resin or  
20 promote its curing, and there may be used, for example, amines, imidazoles, polyfunctional phenols, acid anhydrides and the like. As amines there may be used dicyandiamide, diaminodiphenylmethane, guanylurea and the like. As polyfunctional phenols there may be used hydroquinone, resorcinol, bisphenol A and their halogenated forms, as  
25 well as novolac-type phenol resins and resol-type phenol resins that are condensates with formaldehyde. As acid anhydrides there may be

used phthalic anhydride, benzophenonetetracarboxylic dianhydride, methylhymic acid and the like. As curing accelerators there may be used imidazoles such as alkyl-substituted imidazoles and benzimidazoles.

5 [0026]

The preferred amount of such a curing agent or curing accelerator is, in the case of an amine, an amount such that the equivalents of active hydrogen of the amine and epoxy equivalents of the epoxy resin are approximately equal. For an imidazole as the curing accelerator there is no simple equivalent ratio with active hydrogen, and the required amount is 0.001-10 parts by weight to 100 parts by weight of the epoxy resin. In the case of a polyfunctional phenol or acid anhydride, the required amount is 0.6-1.2 equivalents of phenolic hydroxyl or carboxyl groups with respect to one equivalent of the epoxy resin. A small amount of such a curing agent or curing accelerator will leave some amount of uncured epoxy resin and will lower the T<sub>g</sub> (glass transition temperature), while a large amount will leave some amount of unreacted curing agent and curing accelerator, thereby lowering the insulating property.

20 [0027]

The prepreg can be obtained by preparing a varnish by mixing, dissolving and dispersing a resin composition for prepreg in an organic solvent, and then impregnating it into a fiber material and drying in the present invention. The organic solvent is not particularly restricted so long as it is able to dissolve the resin composition, and as examples there may be mentioned dimethylacetamide,

dimethylformamide, dimethylsulfoxide, N-methyl-2-pyrrolidone,  $\gamma$ -butyrolactone, sulfolane and cyclohexanone.

[0028]

The resin composition for prepreg is preferably the resin composition  
5 containing 100 parts by weight of a polyimide resin and 1-200 parts  
by weight of a thermosetting resin. This will increase the vaporization  
rate of the varnish solvent of the resin composition, making it possible  
to achieve a residual solvent content of 5 wt% or less even at a low  
temperature of below 150°C at which the thermosetting resin curing  
10 reaction is not promoted. As a result, the heat resistance adhesive seal  
have satisfactory adhesion between the fiber base material and copper  
foil. Since the highly heat resistant polyimide resin has siloxane  
structure, the residual solvent can be decreased, the prepreg exhibits  
less swelling due to solvent vaporization during the step of lamination  
15 with the copper foil, and has excellent soldering heat resistance.

[0029]

The prepreg can be fabricated by impregnating the fiber base material  
with the resin composition varnish and drying it in a temperature  
range of 80-180°C. The fiber base material is not particularly  
20 restricted so long as it is one used for fabrication of metal foil-clad  
laminates and multilayer printed circuit boards, and there may be  
mentioned fiber base materials such as woven fabrics and nonwoven  
fabrics. As materials for the fiber base material there may be  
mentioned inorganic fibers such as glass, alumina, asbestos, boron,  
25 silica-alumina glass, silica glass, tirano, silicon carbide, silicon nitride  
and zirconia, organic fibers such as aramid, polyetherether ketone,

polyetherimide, polyethersulfone, carbon and cellulose, and blended systems thereof, among which woven fabrics of glass fibers are preferred. Among these, glass cloths with a thickness of 5-50  $\mu\text{m}$  are preferred as fiber base materials to be used in prepregs. By using a glass cloth with a thickness of 5-50  $\mu\text{m}$  and using the resin composition of the present invention, it is possible to obtain a printed circuit board that can be folded as desired, and which undergoes minimal dimensional change with the temperature and humidity of the manufacturing process.

[0030]

The manufacturing conditions for the prepreg are not particularly restricted, but preferred are conditions wherein at least 80 wt% of the solvent used in the varnish of the resin composition of the present invention evaporates. The fabrication process and drying conditions are also not particularly restricted, and for example, the temperature for drying may be 80-180°C, and the time may be adjusted in balance with the varnish gelling time.

[0031]

The impregnating amount of varnish of the resin composition is preferably such for a varnish solid content of 30-80 wt% with respect to the total amount of solid varnish and fiber base material.

[0032]

The manufacturing methods of insulating boards, laminates and metal foil-clad laminates are as follows. The prepreg of the present invention may be used alone or a plurality thereof laminated into a laminate, stacked with a metal foil on either or both sides as necessary,

and subjected to hot pressure molding at a temperature in the range of 150-280°C or preferably 180-250°C, and a pressure in the range of 0.5-20 MPa or preferably 1-8 MPa, to fabricate an insulating board, laminate or metal foil-clad laminate. Using a metal foil to obtain metal foil-clad laminate, a printed circuit board can be obtained by forming a circuit to it.

[0033]

The metal foils used in the present invention include copper foils and aluminum foils, these metal foils having thicknesses of 5-200  $\mu\text{m}$  which are generally used to laminate can be applied. The metal foil may be a composite foil with a three-layer structure provided with an interlayer made of nickel, nickel-phosphorus, nickel-tin alloy, nickel-iron alloy, lead, lead-tin alloy or the like, having a 0.5-15  $\mu\text{m}$  copper layer and a 10-300  $\mu\text{m}$  copper layer on either side, or a composite foil with a two-layer structure comprising aluminum and copper foils.

[Examples]

[0034]

The present invention will now be explained by examples, but the invention is in no way limited to these examples.

(Synthesis Example 1)

In a 1-liter separable flask there were placed 31.0 g (0.10 mol) of 3,3',4,4'-diphenylethertetracarboxylic dianhydride, 200 g of NMP (N-methyl-2-pyrrolidone) and 200 g of m-xylene, and the mixture was stirred at room temperature (25°C). Next, 34.4 g (0.04 mol) of the reactive silicone oil KF-8010 (trade name of Shin-Etsu Chemical Co., Ltd., amine equivalents: 430) as a siloxanediamine was added

dropwise using a dropping funnel. The reaction mixture was stirred while cooling on ice, and then 24.6 g (0.06 mol) of BAPP (2,2-bis[4-(4-aminophenoxy)phenyl]propane) was added as an aromatic diamine and stirring was continued for 2 hours at room temperature to obtain polyamic acid. The polyamic acid solution was heated to 190°C and then heated and stirred for 20 hours, and the water produced with imide ring closure was removed by azeotropic distillation with m-xylene. Upon completion of the reaction, an NMP solution containing a polyimide resin was obtained.

[0035]

(Synthesis Example 2)

In a 1-liter separable flask there were placed 29.4 (0.10 mol) of 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 200 g of NMP (N-methyl-2-pyrrolidone) and 200 g of m-xylene, and the mixture was stirred at room temperature. Next, 34.4 g (0.04 mol) of the reactive silicone oil KF-8010 (trade name of Shin-Etsu Chemical Co., Ltd., amine equivalents: 430) as a siloxanediamine was added dropwise using a dropping funnel. The reaction mixture was stirred while cooling on ice, and then 24.6 g (0.06 mol) of BAPP (2,2-bis[4-(4-aminophenoxy)phenyl]propane) was added as an aromatic diamine and stirring was continued for 2 hours at room temperature (25°C) to obtain polyamic acid. The polyamic acid solution was heated to 190°C and then heated and stirred for 20 hours, and the water produced with imide ring closure was removed by azeotropic distillation with m-xylene. Upon completion of the reaction, an NMP solution containing a polyimide resin was obtained.

[0036]

(Example 1)

After mixing 265.0 g of an NMP solution of the polyimide resin obtained in Synthesis Example 1 (30.2 wt% solid resin content), 40.0 g of NC3000 (trade name of Nippon Kayaku Co., Ltd.) as an epoxy resin (dimethylacetamide solution with 50 wt% resin solid content) and 0.2 g of 2-ethyl-4-methylimidazole, the mixture was stirred for about 1 hour until uniformity of the resin. It was then allowed to stand for 24 hours at room temperature (25°C) for defoaming to produce a resin composition varnish.

[0037]

(Example 2)

After mixing 216.8 g of an NMP solution of the polyimide resin obtained in Synthesis Example 2 (36.9 wt% solid resin content), 40.0 g of NC3000 (trade name of Nippon Kayaku Co., Ltd.) as an epoxy resin (dimethylacetamide solution with 50 wt% resin solid content) and 0.2 g of 2-ethyl-4-methylimidazole, the mixture was stirred for about 1 hour until uniformity of the resin. It was then allowed to stand for 24 hours at room temperature (25°C) for defoaming to produce a resin composition varnish.

[0038]

(Example 3)

After mixing 248.3 g of an NMP solution of the polyimide resin obtained in Synthesis Example 1 (30.2 wt% solid resin content), 50.0 g of DER331L (trade name of Dainippon Ink & Chemicals, Inc.) as an epoxy resin (dimethylacetamide solution with 50 wt% resin solid

content) and 0.25 g of 2-ethyl-4-methylimidazole, the mixture was stirred for about 1 hour until uniformity of the resin. It was then allowed to stand for 24 hours at room temperature (25°C) for defoaming to produce a resin composition varnish.

5 [0039]

(Fabrication of prepreg and metal foil-clad laminate)

Each of the resin composition varnishes prepared in Examples 1-3 was impregnated into a glass cloth with a thickness of 0.028 mm (trade name 1037 of Asahi Shwebel Co., Ltd.), and then heated at  
10 150°C for 15 minutes for drying to obtain a prepreg with a 70 wt% resin portion. A 12 µm-thick electrolytic copper foil (trade name: F2-WS-12 by Furukawa Electric Co., Ltd.) was stacked onto both sides of the prepreg with the adhesive sides facing the prepreg, and subjected to pressing conditions of 200°C, 90 min, 4.0 MPa to fabricate a  
15 double-sided copper clad laminate.

[0040]

(Comparative Example 1)

The resin composition varnish of Example 1 was used for impregnation into a glass cloth with a thickness of 0.10 mm (100 µm)  
20 (trade name 7010 of Nitto Boseki Co., Ltd.), and was then heated at 150°C for 25 minutes for drying to obtain a prepreg with a 70 wt% resin portion. A 12 µm-thick electrolytic copper foil (trade name: F2-WS-12 by Furukawa Electric Co., Ltd.) was stacked onto both sides of the prepreg with the adhesive sides facing the prepreg, and subjected  
25 to pressing conditions of 200°C, 90 min, 4.0 MPa to fabricate a



double-sided copper clad laminate. The obtained double-sided copper clad laminate was used for the following evaluation.

[0041]

(Evaluations)

- 5 (1) The copper foil peel strength of the double-sided copper clad laminate was measured.
- (2) Upon immersion for 5 minutes in soldering baths at 260°C, 288°C and 300°C, abnormalities such as swelling or peeling were observed.  
○: No abnormalities, × Abnormalities.
- 10 (3) The copper foil was etched for removal and the laminate was folded to evaluate the pliability.  
○: No fracture, × Fracture.
- (4) A circuit was formed on the double-sided copper clad laminate to prepare a daisy chain pattern test piece. Each test piece was subjected  
15 to 1000 cycles of a heat shock test with each cycle being -65°C/30 min, 125°C/30 min, and the change in resistance was measured.  
○: No greater than 10% resistance change, ×: Greater than 10% resistance change.

The obtained results are shown in Table 1.

20 [0042]

[Table 1]

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Evaluation	Units	Example 1	Example 2	Example 3	Comp. Example 1
Polyimide resin	-	Synthesis Example 1	Synthesis Example 2	Synthesis Example 1	Synthesis Example 1
Epoxy resin	-	NC3000	NC3000	DER331L	NC3000
Polyimide/epoxy	pts. by wt.	80/20	80/20	75/25	80/20
Pliability	-	○	○	○	×
Soldering heat resistance	-	○	○	○	○
Heat shock test	-	○	○	○	○
Copper foil peel strength	kN/m	1.2	0.9	1.0	1.1

[0043]

All of the prepregs of Examples 1-3 were satisfactory with high values of 0.9-1.2 kN/m for the copper foil peel strength. Also, the soldering heat resistance (260°C soldering, 288°C soldering, 300°C soldering) was 5 minutes or longer at all temperatures, and no abnormalities such as swelling or peeling were observed. In the heat shock test, the resistance change was within 10% at 1000 cycles, indicating satisfactory connection reliability. Also, the pliability was sufficient to allow folding as desired.

[0044]

In contrast, Comparative Example 1 had no pliability, and cracks formed in the glass cloth and resin sections upon folding. Warping was also observed.

[Document Name] Abstract

[Abstract]

[Problem] The present invention provide a printed circuit board with excellent adhesion property, dimensional stability and heat resistance  
5 and the ability to be bent and housed at high density in electronic device packages, as well as to provide a prepreg and metal foil-clad laminate which yield said printed circuit board.

[Means of Solution] A prepreg obtained by impregnating a resin composition comprising a resin with an imide structure and a  
10 thermosetting resin into a fiber base material with a thickness of 5-50  $\mu\text{m}$ .

[Selected Drawing] None